

# Preparation of Some Mixed Diesters of Aliphatic Diols and Their Evaluation as Plasticizers

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## ABSTRACT

Mixed diesters of three diols—ethylene glycol, diethylene glycol, and 2-butene-1,4-diol—were prepared wherein one of the ester moieties was benzoate. The laurates were shown to be excellent plasticizers for polyvinyl chloride (PVC) resin. Diesters containing two aroyl groups, or benzoyl and a short branched-chain alkanoyl group were also shown to be compatible plasticizers for PVC resin. Longer chain acids, including oleic and erucic, gave incompatible plasticizers. Benzoyloxyethoxyethyl laurate plasticized PVC had low temperature properties, volatility, and thermal stability superior to PVC plasticized with di-2-ethylhexyl phthalate.

## INTRODUCTION

Esters of long chain monobasic acids have a low degree of polarity which limits their solvency and compatibility and in general restricts their usage to secondary plasticizers, where enhanced lubricity and improved low temperature properties are needed (1,2). Plasticizers derived from monoether glycols and fatty acids are more compatible than the simple esters. Increased compatibility is obtained by esterification of the long chain acids with short chain polyhydric alcohols, such as ethylene glycol and diethylene glycol. Generally, these fatty acid diesters offer good compatibility when compared with typical dibasic acid esters and have been shown to have good low temperature properties (3,4). This report describes the preparation and evaluation of representative mixed diesters of ethylene glycol, diethylene glycol, and 2-butene-1,4-diol as primary plasticizers for polyvinyl chloride (PVC).

## EXPERIMENTAL PROCEDURES

The ethylene glycol, diethylene glycol, 2-butene-1,4-diol, and acid chlorides were commercial products used without further purification. Acid chlorides not commercially available were prepared in the laboratory from recrystallized fatty acids.

Ethylene glycol monobenzoate was prepared by dropwise addition of benzoyl chloride to ethylene glycol (1:1 molar ratio) maintained below room temperature with an ice bath. Pyridine was used as an HCl scavenger. The product was washed with water and dried over anhydrous sodium sulfate. The monobenzoate was obtained from the mixed product by short pass distillation at 112 C and 1.5-2.0 mm. The diethylene glycol monobenzoate and 4-hydroxy-2-butenyl benzoate were prepared as described above and collected at 158 C and 1.5-2.0 mm and 130 C and 1.5-2.0 mm, respectively. The diesters were prepared by interaction of equimolar quantities of the benzoate half ester and the acid chloride in the presence of excess pyridine using benzene as the solvent. The resulting diesters were water-washed, dried over anhydrous sodium sulfate, and eluted through a column packed with activated alumina to remove residual free acids. The solvent was removed at reduced pressure. The final products were characterized by nuclear magnetic resonance and infrared spectral analyses. Densities were determined pycnometrically in a thermostated bath controlled to  $\pm 0.1^\circ\text{C}$ . Refractive indices were

measured at  $30 \pm 1^\circ\text{C}$  with a precision Bausch and Lomb refractometer.

The diesters were screened as plasticizers for vinyl chloride homopolymer (Geon 101) and compared with a control plasticizer, di-2-ethylhexyl phthalate (DOP). The formulation employed was as follows: resin, 63.5%; plasticizer, 35%; basic lead carbonate stabilizer, 1.0%; stearic acid, 0.5%. Milling, molding, and testing procedures were those described by Magne et al (5). Volatilities were determined by the activated carbon method (6). Thermal stabilities were established in terms of the reflectances of the plasticized stock after subjection to increasing exposure periods in a forced draft oven maintained at 176 C. These values were determined by means of a "Photoelectric Reflection Meter Model 610," using the amber  $0^\circ$ ,  $45^\circ$  directional reflectance. Compositions which showed no signs of exudation during 90 days of shelf storage were rated compatible.

## RESULTS AND DISCUSSION

The plasticizer evaluation data presented in Table I relate the influence of the alkanoyl and aroyl substituents on the diol to the plasticizer properties of the compound. Each of the diols—ethylene glycol, diethylene glycol, and 2-butene-1,4-diol—is esterified to a benzoate moiety and another functional group. If the benzoate group is assumed to be a stabilizing entity, then the plasticizing character of the compounds can be observed in terms of the secondary substituent. The diols chosen contributed little to enhance the compatibility of esters palmitate, oleate, and erucate. All of the long chain esters, with the exception of the laurate and the 12-acetoxyoleate, were incompatible; either they did not mill initially (erucate) or they bled from the molded sample on standing for several days (palmitate and oleate). The lauroyl esters of the monobenzoates of all three diols were compatible; in fact, the diglycol ester had extremely good properties. The volatility of the glycol and butene diol esters was higher than desirable (3.24 and 3.40%), but these esters had acceptable low temperature properties (brittle points of -44 and -41 C). On the other hand, both volatility (1.61%) and brittle point (-46 C) were good for benzoyloxyethoxyethyl laurate. The thermal stability of the three laurates differed, depending on the diol used. The 4-benzoyloxy-2-butenyl laurate darkened considerably during the 1st hr, whereas the benzoyloxyethyl laurate and benzoyloxyethoxyethyl laurate exhibited thermal stability exceeding that of DOP, as is shown in Figure 1. Benzoyloxyethoxyethyl laurate compared well with DOP and was better than benzoyloxyethyl laurate in tensile strength, 100% modulus, and elongation at break. Tests for these properties were not determined for the 4-benzoyloxy-2-butenyl laurate.

Introduction of the acetoxy group (benzoyloxyethyl 12-acetoxyoleate and benzoyloxyethoxyethyl 12-acetoxyoleate) into the long chain improved compatibility and low temperature properties of both the glycol and diglycol esters. The 12-acetoxy derivative was not prepared for the butene diol. Tensile measurements for the two acetoxyoleates compared well with those of DOP, but volatility and thermal stability were unfavorable.

Aroyl-substituted diglycol monobenzoates—namely, benzoyloxyethoxyethyl benzoate, 2-furoate, and *p*-

TABLE I  
Physical Properties and Plasticizer Characteristics of Diester-Plasticized Polyvinyl Chloride (35% Plasticizer)

Sample no.	Plasticizer	Compatibility <sup>a</sup>	Tensile strength (psi)	100% Modulus (psi)	Elongation (%)	Brittle point (C)	Volatility loss (%)	Density <sup>b</sup> (30 C)	Refractive index <sup>b</sup> (n <sub>D</sub> <sup>30</sup> )
1	Benzoyloxyethyl laurate	C	2114	1702	262	-44	3.24	1.0034	1.4830
2	Benzoyloxyethyl palmitate	I	-	-	-	-	-	- <sup>c</sup>	-
3	Benzoyloxyethyl oleate	I	-	-	-	-	-	0.9754	1.4849
4	Benzoyloxyethyl 12-acetoxyoleate	C	2890	1578	336	-34	2.71	0.9907	1.4772
5	Benzoyloxyethyl erucate	I	-	-	-	-	-	0.9496	1.4820
6	Benzoyloxyethoxyethyl benzoate	C	3498	1864	333	-10	3.61	1.1677	-
7	Benzoyloxyethoxyethyl 2-furoate	C	3519	2198	336	-11	1.61	1.2122	-
8	Benzoyloxyethoxyethyl <i>p</i> -toluoaate	C	3356	1755	337	-12	2.87	1.1554	-
9	Benzoyloxyethoxyethyl trimethylacetate	C	-	-	-	-20	-	1.0684	-
10	Benzoyloxyethoxyethyl laurate	C	3301	1723	222	-46	1.14	0.9869	1.4740
11	Benzoyloxyethoxyethyl palmitate	I	-	-	-	-	-	0.9893	-
12	Benzoyloxyethoxyethyl oleate	I	-	-	-	-	-	0.9868	1.4852
13	Benzoyloxyethoxyethyl 12-acetoxyoleate	C	2904	1847	250	-34	8.43	1.0061	1.4770
14	Benzoyloxyethoxyethyl erucate	I	-	-	-	-	-	0.9503	-
15	4-Benzoyloxy-2-butenyl laurate	C	-	-	-	-41	-	0.9685	-
16	4-Benzoyloxy-2-butenyl palmitate	I	-	-	-	-	-	0.9554	-
17	4-Benzoyloxy-2-butenyl oleate	I	-	-	-	-	-	0.9968	-
18	4-Benzoyloxy-2-butenyl erucate	I	-	-	-	-	-	1.0632	-
19	4-Benzoyloxy-2-butenyl trimethylacetate	C	-	-	-	-24	-	1.0631	-
20	4-Benzoyloxy-2-butenyl hydrocinamate	C	-	-	-	-18	-	1.1262	-
21	Di-2-ethylhexyl phthalate (control)	C	3082	1785	349	-31	1.62	-	-

<sup>a</sup>C = compatible, I = incompatible.

<sup>b</sup>Of diester plasticizer.

<sup>c</sup>mp 68 C.

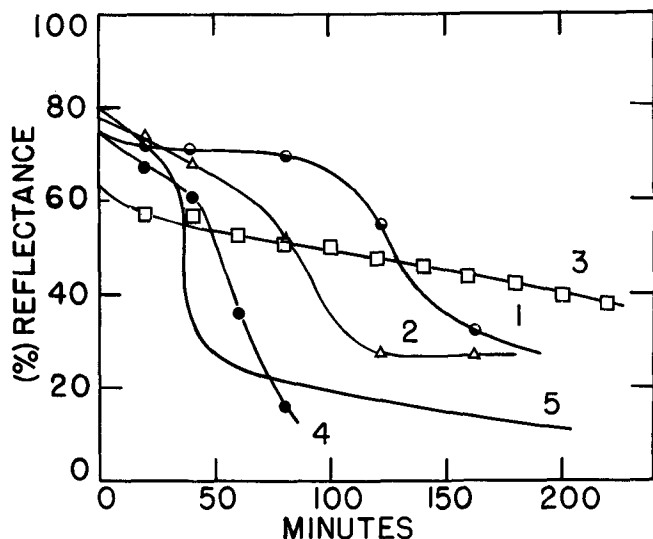


FIG. 1. Thermal stability of diester compositions with polyvinyl chloride (standard formulation). Curve 1 = benzoyloxyethyl laurate (○); curve 2 = benzoyloxyethoxyethyl *p*-toluate (△); curve 3 = benzoyloxyethoxyethyl laurate (□); curve 4 = 4-benzoyloxy-2-butenyl laurate (●); curve 5 = di-2-ethylhexyl phthalate (DOP) (—).

toluate—were all compatible plasticizers for PVC. Brittle points of -10, -11, and -12 C and volatilities of 3.61, 1.61,

and 2.87% were observed. Tensile strength, 100% modulus, and elongation at break were comparable to those of DOP. Only the benzoyloxyethoxyethyl *p*-toluate had acceptable thermal stability (Fig. 1). The others darkened rapidly in the 1st hr.

The trimethylacetyl ester of the diglycol and 2-butene-1,4-diol, as well as the 4-benzoyloxy-2-butenyl hydrocinnamate, showed good compatibility, with brittle points ranging from -18 to -24 C. No tensile, thermal stability, or volatility measurements were made on these samples.

Alkanoyl aryl esters of diols appear to have severe limitations as a general class of plasticizers for PVC resins. However, in this class of compounds, plasticizers with good low temperature properties, volatility, and thermal stability are available through judicious choice of diol and alkanoyl moiety.

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